Photoacoustic studies of $Cd_{1-x}Be_xSe$ mixed crystals

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In presented paper we report the photoacoustic investigations of $Cd_{1-x}Be_xSe$ mixed crystals. The investigated samples were grown by the high pressure Bridgman method with different concentration of Be ($0.1<x<0.2$). For investigation of continues wave photoacoustic spectra a piezoelectric transducer (PZT) and an open cell were used. The increase of the energy gap with increasing x value has been observed. The values of thermal diffusivity were estimated using the dependence of amplitude and phase of PA signal on light modulation frequency.

1. Introduction

The interest in wide gap ternary and quaternary II-VI semiconductor solid solution is for their possible applications in optoelectronics [1]. Up to date the blue-green II-VI laser structures based on ZnSe and ZnCdSe are grown mainly on GaAS [2].
ZnSe-based compounds are responsible for slow degradation of light-emitting diodes [3] and short lifetime of electroluminescent devices [4]. Recently a new CdBeSe alloy was proposed to be used as an active layer material in green semiconductor lasers instead of ZnCdSe [5].

Because of dominant covalent bonding and high cohesive energy of BeSe, a noticeable lattice strengthening of CdBeSe as compared to ZnCdSe is expected and a possibility to obtain lattice-matched material to GaAs and ZnSe structures. [6,7]. Until now the study are focused mainly on MBE growth of $Cd_{1-x}Be_xSe$ but the physical properties of respective bulk compounds remain almost unknown. [8].
For MBE grown $Cd_{1-x}Be_xSe$ samples, the best optical and structural properties have been observed in the vicinity of x = 0.46 [9]. Estimated band gap bowing parameter for MBE grown samples is about 3 eV and indicates the strong bowing [5].
In this paper we present the preliminary results of photoacoustic and photoluminescence measurements of $Cd_{1-x}Be_xSe$ crystals grown from CdSe, Be, Se melt by the modified Bridgman method.

2. Experimental

The investigated samples were grown by the high-pressure Bridgman method under argon overpressure (14 MPa). The crystals were cut into 1-1,5 mm thick plates, mechanically polished and chemically etched. The investigated crystals plates exhibit a wurtzite – type structure.
Photoacoustic (PA) measurements were carried out using an open cell. The 300 W Cermax xenon short are lamp operating in the range from λ=350 nm to λ=600 nm and

SPM –2 monochromator were applied as radiation source for PA measurements. The thermal diffusivity values for $Cd_{1-x}Be_xSe$ were calculated using PA signal dependence on modulation frequency.

Luminescence spectra were measured under He-Cd laser (325 nm) excitation in the temperature range from 33 K to room temperature in the spectral range from 350 nm to 800 nm.

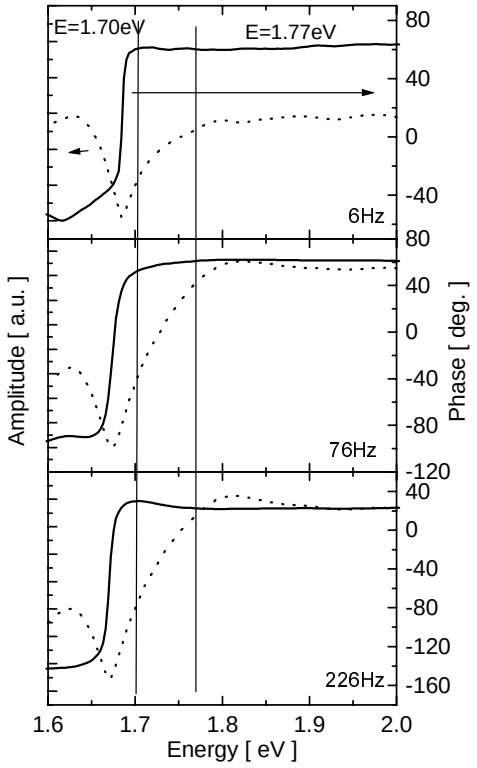

Figure 1: Phase (solid) and amplitude (dots) spectra of CdSe for different modulation frequencies

3. Results

Photoacoustic experiments were performed for pure CdSe and the samples of $Cd_{1-x}Be_xSe$ mixed crystals for $x = 0.1$ and $x = 0.2$. Fig. 1 shows the spectra of CdSe at three different frequencies. Two maxima are observed for low and high regions in the energy range 1.6-1.75 eV. The maximum in the sub-band-gap region is observed for all the frequencies and predicted by Jackson-Amer theory. When exciting beam falls on the sample and the transducer is situated behind it, the amplitude of the signal goes to zero at $\alpha l = 2$, where the compensation due to the bending equals the expansion due to the heating. However the position of that peak doesn't change with the increase of modulation frequency as is predicted by J-A theory. The ratio of intensities of the peaks in the high and low absorption regions decreases with increasing of modulation frequency.

Since the general expression for the PA signal is complicated, it not easy to find the relation between the amplitude and phase of PA signal and the absorption coefficient. In the past we considered the case of thermally thin but optically thick sample. This method however was correct for the spectra were a saturation or amplitude decrease appears in the high absorption region. In the observed phase spectra, the value of the phase signal in high absorption region becomes constant for the value of energy corresponding to

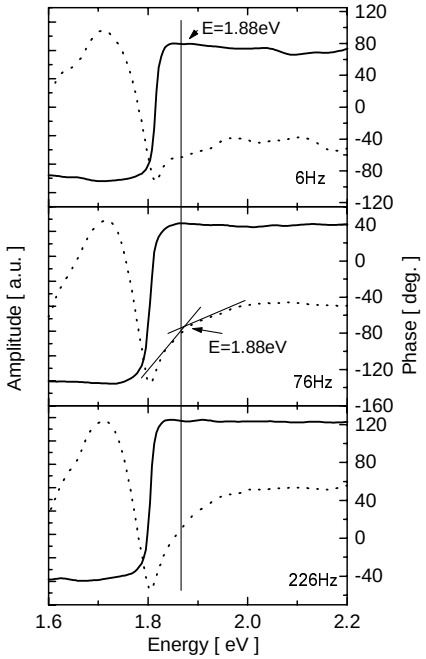

Figure 2: Phase (solid) and amplitude (dots) spectra of $Cd_{1-x}Be_xSe$ ($x = 0.1$), sample *a* for different modulation frequencies

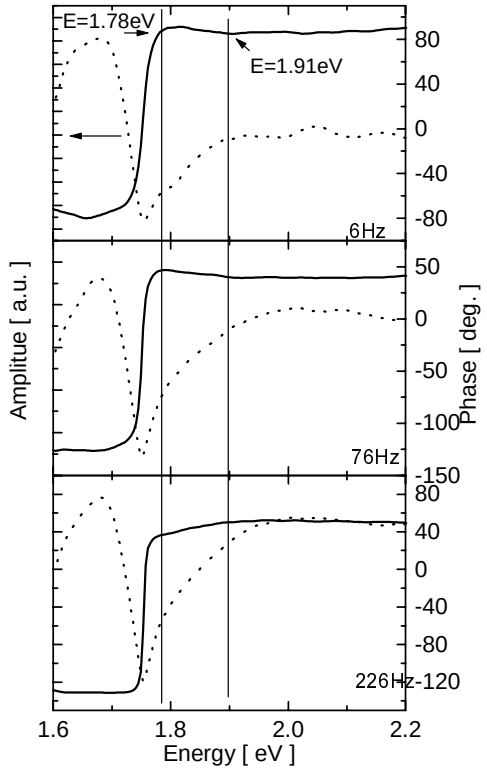

Figure 3: Phase (solid) and amplitude (dots) spectra of $Cd_{1-x}Be_xSe$ (*x=0.1*), sample *b* for different modulation frequencies

bending point was observed in the amplitude spectra for this energy value. The different character of the phase spectra was observed for the sample *b*. Two characteristic points could be singled out for energies E=1.78eV and E=1.91eV. The second value corresponds to the energy gap. As it was observed for the CdSe that region could be associated with the absorption edge.

Fig 4. shows the amplitude and phase spectra of $Cd_{1-x}Be_xSe$ sample with beryllium content of 20% in the ingot. Two characteristic points could also be singled out for energies E=1.81eV and E=1.93eV. The second value is the value of the energy gap.

energy gap. This feature was used for determination of E_g value. For CdSe the energy gap was estimated as $E_g=1.77eV$, which is in good agreement with literature data.

At the energy of E=1.70eV the bending point - the change of the slope in amplitude spectra can be seen. As observed for $Cd_{1-x}Mn_xTe$ [10], the change of the phase value could be associated with the change of the character of photoacoustic signal generation. The observed features of experimental curves in the energy range $1.70\ eV<E<1.77\ eV$ could be associated with the absorption edge – Urbach tail.

There were measured two samples with Beryllium content of 10% in the ingot (starting material). Their amplitude and phase spectra for different modulation frequencies are presented in Fig.2 (sample a) and Fig. 3 (sample b) respectively. The value of energy gap for the sample *a* was determined as $E_q=1.88eV$. The

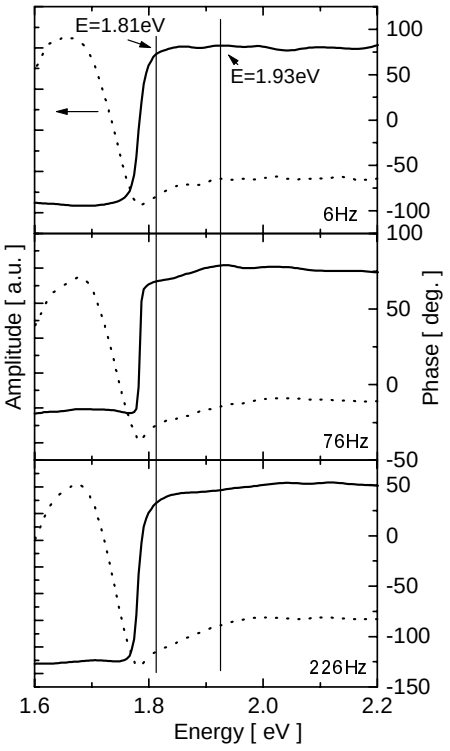

Figure 4: Phase (solid) and amplitude (dots) spectra of $Cd_{1-x}Be_xSe$ (x=0.2) for different modulation frequencies

It was found that in the investigated composition the energy gap increases with increase of beryllium content.

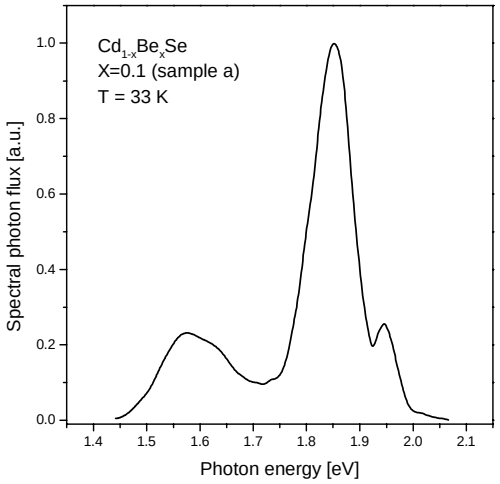

Figure 5: Luminescence spectra of $Cd_{1-x}Be_xSe$ (x=0.1), sample *a* for temperature T=33K

Fig. 5 gives the PL spectrum of $Cd_{0.92}Be_{0.075}Se$ at T=38 K. The high – energy part of spectrum exhibit two peaks positioned at 1.956 eV and 1.85 eV. The second one is thermally quenched at temperature higher than about 100 K and it is interpreted as an "edge emission" due to recombination of shallow donor-acceptor pairs. The first line shifts monotonically towards lower energies with increasing temperature and is observed up to room temperature so it is interpreted as exiton emission. Its maximum at room temperature appears at energy 1.866 eV which very well corresponds to the ellipsometric data (1.865 eV).

Because of the photoacoustic signal depends on heat diffusion in the sample, it is possible to use the PA method to investigate thermal properties of semiconductors. Thermal diffusivity measures the rate of the heat diffusion in the material and it is an unique parameter like the absorption coefficient. The thermal diffusivity values for $Cd_{1-x}Be_xSe$ were determined using photoacoustic amplitude and phase signal dependence on modulation frequency. The model developed by Blonskij et. al. was applied [11]. These authors averaged the thermal diffusion equations over the area of the sample, solved the thermoelastic problem and gave the analytical expressions for the amplitude and phase., namely:

$$|V| = \frac{P\alpha}{kla^2}\psi(al),$$

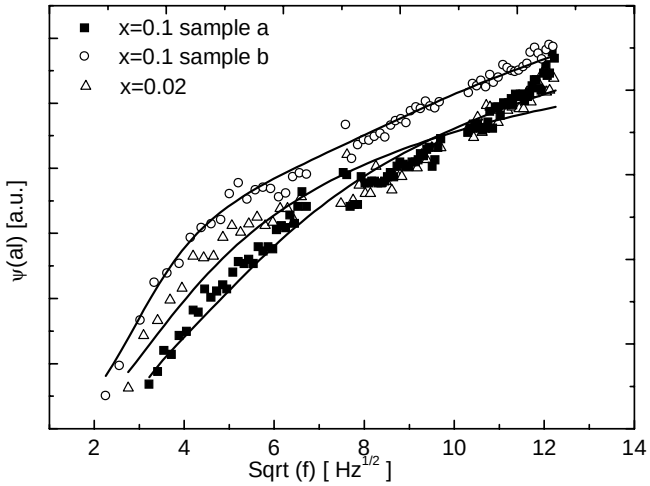

Figure 6: dependence of $\psi(al)$ term on square root of modulation frequency for three samples of $Cd_{1-x}Be_xSe$ (*x=0.01* - samples *a* and *b*, *x=0.02*).

$$\psi(\boldsymbol{al}) = \{[1 - \frac{3}{2\boldsymbol{al}} \frac{\sinh(\boldsymbol{al}) + \sin(\boldsymbol{al})}{\cosh(\boldsymbol{al}) + \cos(\boldsymbol{al})}]^2 +$$
$$+ [\frac{3}{2\boldsymbol{al}} \frac{\sinh(\boldsymbol{al}) - \sin(\boldsymbol{al})}{\cosh(\boldsymbol{al}) + \cos(\boldsymbol{al})}]^2\}^{1/2}$$

$$\tan\tilde{\varphi} = \frac{\frac{3}{2\boldsymbol{al}} \frac{\sinh(\boldsymbol{al}) - \sin(\boldsymbol{al})}{\cosh(\boldsymbol{al}) + \cos(\boldsymbol{al})}}{1 - \frac{3}{2\boldsymbol{al}} \frac{\sinh(\boldsymbol{al}) + \sin(\boldsymbol{al})}{\cosh(\boldsymbol{al}) + \cos(\boldsymbol{al})}},$$

where $\boldsymbol{V}, \varphi$ are signal amplitude and phase, respectively, α - absorption coefficient, $\boldsymbol{k}$ - thermal conductivity, $\boldsymbol{l}$ - sample thickness, $\boldsymbol{P}$ - constant, $\boldsymbol{a} = \sqrt{\omega / 2\boldsymbol{D}}$, $\omega = 2\pi\boldsymbol{f}$, $\boldsymbol{f}$ - modulation frequency, $\boldsymbol{D}$ - thermal diffusivity.

Fig 6 shows the dependence of $\psi(\boldsymbol{al})$ term on square root of modulation frequency for three samples of $Cd_{1-x}Be_xSe$ (*x=0.1*, samples *a* and *b*, x=0.02). The CdSe sample with known value of thermal diffusivity (*D=0.061 cm²/s*) was used to calibrate the method. The obtained values of the thermal diffusivities are *D=0.02 cm²/s* for $Cd_{1-x}Be_xSe$ (*x=0.01*, sample *a*), *D=0.09 cm²/s* for $Cd_{1-x}Be_xSe$ (*x=0.01*, sample b) and *D=0.01 cm²/s* for $Cd_{1-x}Be_xSe$ (*x=0.02*)

As the experiment setup used in our experiment differs a little from the one used in Blonskij model, a modification of the experiment is in progress in order to improve the accuracy of measurements.

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